VIBRATIONAL SPECTRA OF THE THREE ISOMERIC DINITROBENZENES

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ABSTRACT. The infrared absorption spectra of the three isomeric dinitrobenzenes have been recorded in the region 700-4000 cm^{-1} on a Perkin-Elmer double beam infrared spectrophotometer (Model 13-U) with NaCl prism using KBr pellet technique. The vibrational assignments of the observed frequencies have been made by assuming C_{2v} point group for *o*-and *m*-dinitrobenzenes and $D_{2h} = V_h$ point group for *p*-dinitrobenzene.

INTRODUCTION

A considerable amount of data has been published on the N – O stretching vibrations of the nitro group (Brown 1955; Kross and Fassel 1956). The vibrational spectrum of nitrobenzene has been investigated by Green *et al* (1961), who have proposed assignments of vibrational frequencies to various modes of vibration of the molecule. Studies of the infrared spectra of the three isomeric dinitrobenzenes have been made by Katritzky and Simmons (1959), Conduit (1959) and Pristera *et al* (1960), but none of these workers has presented a complete analysis of all the observed bands. Therefore we proposed to study the infrared absorption spectra of the three isomeric dinitrobenzenes. The Raman spectra of these compounds have been reported in the Landolt Bornstein table (1951) without polarisation measurements.

EXPERIMENTAL

The chemicals used were manufactured by B.D.H. These were of pure quality and are solid at room temperature.

The infrared absorption spectra of *o*-, *m*- and *p*-dinitrobenzenes have been recorded in the region 700-4000 cm^{-1} on a Perkin-Elmer double beam infrared spectrophotometer (Model 13-U) with NaCl prism using KBr pellet technique. The pellets were prepared by taking a few milligrams of the substance and mixing it with a small amount of potassium bromide. The mixture was then ground to a fine powder in an agate mortar and pressed in a special die for few minutes under a pressure of about 40 tons per sq. inch in a hydraulic press. The accuracy of measurements is 2 cm^{-1} between 700-1500 cm^{-1}, 4 cm^{-1} between 1500-3000 cm^{-1} and 10 cm^{-1} above 3000 cm^{-1}.

RESULTS AND DISCUSSION

The traces of infrared spectra of the three dinitrobenzenes are given in figures 1, 2, and 3 respectively. The infrared and Raman frequencies alongwith their relative intensities and proposed assignments are given in tables 1, 2 and 3 respectively for the three dinitrobenzenes.

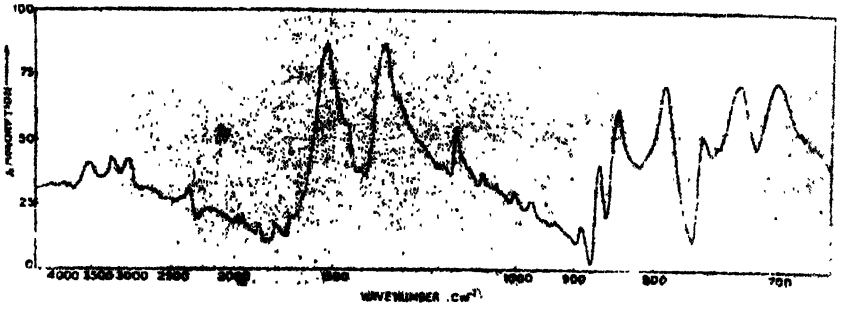

Figure 1. Infrared absorption spectrum of o-dinitro benzene (solid phase)

Figure 2. Infrared absorption spectrum of m-dinitro benzene (solid phase)

Figure 3. Infrared absorption spectrum of p-dinitro benzene (solid phase)

Table 1. Vibrational frequencies and their assignments for *o*-dinitrobenzene

Raman (solution)		Infrared (KBr pellet) present work		Assignment
cm^{-1}	Int.	cm^{-1}	Int.	
685	(0)			a_1 C···C—C i.p. bending
		700	(8)	b_1 fundamental
		727	(8)	b_1 C—C—C o.p. bending
		754	(6)	
		789	(8)	b_1 C—H o.p. bending
		841	(7)	b_1 C—H o.p. bending
858	(1)	864	(5)	a_1 NO_2 i.p. bending
		887	(2)	
915	(1)	924	(2)	b_1 C H o.p. bending
		969	(3)	b_1 C—H o.p. bending
		1000	(3)	a_1 C—C—C i.p. bending
1041	(1)	1041	(4)	a_1 C—C stretching (ring breathing)
		1071	(4)	b_2 C—H i.p. bending
		1148	(6)	a_1 C—H i.p. bending
		1192	(5)	a_1 C- H i.p. bending
		1209	(5)	
		1293	(6)	b_2 C—H i.p. bending
		1319	(8)	a_1 C—N stretching
1361	(5)	1354	(10)	a_1 N = O sym. stretching
		1414	(4)	b_2 C - C stretching
		1456	(6)	a_1 C = C stretching
1537	(0)	1526	(10)	b_2 N = O asym. stretching
1607	(0)	1608	(3)	a_1 C = C stretching
		1639	(2)	A_1 789+841 = 1630
		1662	(2)	B_1 789+864 = 1653
		1742	(2)	B_1 700+1041 = 1741
		1846	(2)	B_1 700+1148 = 1848
		1964	(2)	B_1 924+1041 = 1965
		1998	(2)	A_1 685+1319 = 2004
		2170	(2)	B_1 841+1319 = 2160
		2246	(2)	B_1 789+1456 = 2245
		2374	(3)	B_1 924+1456 = 2380
		2419	(3)	B_1 969+1456 = 2425
		2679	(3)	A_1 1319+1354 = 2673
		2883	(5)	B_2 1354+1526 = 2880
		3099	(5)	b_2 C—H stretching
		3780	(4)	B_2 685+3098 = 3783
		3882	(3)	
		3942	(3)	A_1 1354+1526+1071 = 3951

N.B. : i.p. = in-plane; o.p. = out-of-plane; sym. = symmetric and asym. = asymmetric

Table 2. Vibrational frequencies and their assignments for *m*-dinitrobenzene

Raman (solution)		Infrared (KBr pellet) present work		Assignment
cm^{-1}	Int.	cm^{-1}	Int.	
		683	(10)	a_1 C—C– C i.p. bending
702	(0)			
		724	(9)	b_1 C– C –C o.p. bending
		760	(2)	
		791	(2)	b_1 C– –H o.p. bending
		817	(7)	b_1 C– –H o.p. bending
840	(3)	837	(6)	a_1 NO_2 i.p. bending
909	(0)	915	(7)	b_1 C– H o.p. bending
		944	(2)	b_1 C – H o.p. bending
1005	(4)	1003	(5)	a_1 C—C stretching (ring breathing)
		1027	(4)	a_1 C–C – C i.p. bending
		1067	(8)	b_2 C – H i.p. bending
		1092	(6)	
		1128	(4)	
1149	(9)	1145	(5)	a_1 C—H i.p. bending
		1172	(5)	a_1 C—H i.p. bending
1210	(1)	1212	(5)	
		1273	(7)	b_2 C– –H i.p. bending
1353	(0)	1347	(8)	a_1 C–N stretching
1365	(3)	1357	(10)	a_1 N = O sym. stretching
1440	(0)	1441	(5)	b_2 C = C stretching
		1476	(7)	a_1 C = C stretching
		1510	(9)	b_2 C = C stretching
1538	(4)	1530	(10)	b_2 N = O asym. stretching
1600	(3)	1603	(7)	b_1 C = C stretching
		1694	(1)	A_1 791+915 = 1706
		1758	(1)	B_1 724+1027 = 1751
		1820	(1)	A_1 2×915 = 1830
		1904	(2)	B_1 724+1172 = 1896
		1996	(2)	A_1 2×1003 = 2006
		2252	(3)	B_1 915+1347 = 2262
		2359	(3)	A_1 1003+1357 = 2360
		2383	(3)	A_1 1027+1357 = 2384
		2431	(3)	B_2 1067+1357 = 2424
		2492	(3)	A_1 1146+1347 = 2493
		2888	(5)	B_2 1357+1530 = 2887
		3099	(6)	b_2 C—H stretching
		3461	(5)	B_2 1027+1357+1067 = 3451
		3574	(2)	B_2 1067+1357+1146 = 3570
		3928	(4)	B_2 837+3099 = 3936

N.B. : i.p. = in-plane; o.p. = out-of-plane; sym. = symmetric; and asym. = asymmetric.

Table 3. Vibrational frequencies and their assignments for *p*-dinitrobenzene

Raman (solution)		Infrared (KBr pellet) present work		Assignment
cm^{-1}	Int.	cm^{-1}	Int	
		710	(8)	b_{3u} C–H o.p. bending
		784	(2)	
		800	(3)	b_{3u} C–H o.p. bending
		820	(4)	
		839	(8)	b_{1g} NO_2 i.p. bending
		873	(7)	b_{1u} NO_2 i.p. bending
906	(0)			b_{2g} C—H o.p. bending
		1010	(4)	b_{2u} C—C–C i.p. bending
		1104	(5)	b_{2u} C—H i.p. bending
1106	(1)			a_{1g} C—C stretching (ring breathing)
		1144	(2)	
		1161	(3)	b_{1u} C—H i.p. bending
		1181	(3)	
		1213	(3)	
		1270	(5)	
		1282	(5)	b_{1u} C = C stretching
		1319	(9)	b_{2u} C—N stretching
		1343	(10)	b_{2u} N = O sym. stretching
1358	(4)			b_{3g} C—H i.p. bending
		1382	(5)	b_{2u} C = C stretching
		1407	(3)	
		1478	(4)	b_{1u} C = C stretching
		1552	(9)	b_{1u} N = O asym. stretching
1585	(1)	1580	(6)	a_{1g} C = C stretching
		1627	(2)	B_{1u} 710+906 = 1616; $b_{3u} \times b_{2g} = B_{1u}$
		1699	(1)	B_1 800×906 = 1706; $b_{3u} \times b_{2g} = B_{1u}$
		1800	(1)	
		1942	(2)	
		2205	(2)	B_{2u} 1104+1106 = 2210; $b_{2u} \times e_g = B_{2u}$
		2262	(2)	B_{1u} 1106+1161 = 2267; $e_g \times b_{1u} = B_{1u}$
		2360	(3)	B_{1u} 1010+1358 = 2368; $b_{2u} \times b_{3g} = B_{1u}$
		2462	(1)	B_{1u} 1104+1358 = 2462; $b_{2u} \times b_{3g} = B_{1u}$
		2840	(4)	B_{2u} 1358+1478 = 2836; $b_{3g} \times b_{1u} = B_{2u}$
		2921	(4)	B_{2u} 1343+1580 = 2923; $b_{2u} \times e_g = B_{2u}$
		3109	(5)	b_{2u} C—H stretching
		3474	(5)	
		3817	(4)	
		3924	(5)	
		3974	(4)	

N.B. : i.p. = in-plane; o.p. = out-of-plane; sym. = symmetric and asym. = asymmetric.

In assigning the bands to various modes of vibration assistance has been taken from the assignments of nitrobenzene (Green *et al* 1961; Stephenson *et al* 1961), halogenonitrobenzenes (Mooney, 1964) and other disubstituted benzenes (Shurvell *et al* 1966; Singh *et al* 1965).

o-Dinitrobenzene

Assuming the "NO_2" groups to behave as a single particle and lie in the plane of the ring, the molecule *o*-dinitrobenzene belongs to point group C_{2v}. As recommended by the Joint Commission for Spectroscopy (Mulliken, 1955), the *z*-axis is chosen as the two-fold axis (passing through the bond between carbon atoms 1 and 2). The thirty fundamentals then divide among the symmetry species of the group as follows: $(11a_1+10b_2)$ in-plane modes and $(5a_2+4b_1)$ out of-plane modes. All fundamentals are Raman active and all, except the a_2 vibrations are infrared active. Besides these thirty vibrations, there would be 12 internal vibrations due to two NO_2 groups, thus giving 42 vibrations in all.

Four C-H stretching modes, two of symmetry a_1 and two of symmetry b_2, are expected between 3000 and 3100 cm^{-1}. Only one frequency, 3098 cm^{-1} is observed in the infrared spectrum of this compound in this region and is arbitrarily assigned to b_2 C-H stretching mode.

The infrared peak at 1608 cm^{-1} is assigned to a_1, C = C stretching mode. This vibration originates from the degenerate e_{2g} (1585 cm^{-1}) vibration of benzene. In *o*-dichlorobenzene, both components were assigned to a single peak at 1576 cm^{-1} (Scherer and Evans, 1963). Two medium strong infrared peaks, 1456 and 1414 cm^{-1}, correspond to the 1485 $cm^{-1}(e_{1u})$ C = C stretching vibration in benzene. The peak, 1041 cm^{-1} observed with medium intensity in the infrared spectrum and weak intensity in the Raman spectrum is assigned to ring breathing mode corresponding to 992 cm^{-1} (a_{1g}) vibration of benzene. Venkateswarlu and Radhakrishnan (1962) have assigned the frequencies 1041, 1052 and 1044 cm^{-1} in *o*-dichloro-benzene, *o*-xylene and *o*-cresol respectively to ring breathing mode.

The four infrared frequencies 1293, 1192, 1148 and 1071 cm^{-1} have been assigned to C-H in-plane bending modes. The corresponding frequencies for *o*-dichlorobenzene (Scherer and Evans, 1963) are 1252, 1162, 1140 and 1081 cm^{-1}.

Similarly the four C-H out-of-plane bending frequencies are usually found between 700 and 1000 cm^{-1} in the vibrational spectra of *o*-disubstituted benzenes. Thus the frequencies 696, 924, 841 and 789 cm^{-1} are assigned to C-H out-of-plane bending modes.

Besides these frequencies, the spectrum of *o*-dinitrobenzene should also contain frequencies due to vibrations of the NO_2 group. The frequencies 1526 and 1354 cm^{-1} observed with strong intensities in the infrared spectrum of *o*-dinitrobenzene are assigned to the asymmetric and symmetric N = O stretching modes respectively. The strong occurrence of these two bands and their assignment

to NO_2 vibration is supported by the assignment of symmetrical and asymmetrical stretching modes at 1345 and 1517 cm^{-1} by Stephenson *et al* (1961) and at 1357 and 1550 cm^{-1} by Green *et al* (1961) in nitrobenzene. These two bands are quite strong, better than phenyle vibration in this region. Rao (1963) has also marked for the strong occurrence of these vibrations. The three isomeric fluoro nitrobenzenes studied by Medhi (1964) show strong NO_2 vibration. The frequency 1319 cm^{-1} is assigned to C-N stretching mode and the frequency 864 cm^{-1} is assigned to NO_2 in-plane bending mode.

m-Dinitrobenzene

The molecule belongs to the same point group (C_{2v}) as the *o*-isomer, but in this case the two fold axis passes through carbon atoms 2 and 5. The thirty fundamentals divide among the symmetry species of the group as follows : $(11a_1+10b_2)$ in-plane vibrations and $(3a_2+6b_1)$ out-of-plane modes. Again, all fundamentals are Raman active and all, except the a_2 vibrations are infrared active.

The frequency 3099 cm^{-1} observed with strong intensity in the infrared spectrum of *m*-dinitrobenzene is assigned to b_2 C-H stretching mode. The assignment of the C = C stretching modes to the four frequencies 1603, 1510, 1476 and 1441 cm^{-1} is straight-forward. The corresponding frequencies for *m*-dichlorobenzene (Scherer and Evans, 1963) are 1580, 1580, 1464 and 1412 cm^{-1}. The frequency 1003 cm^{-1} observed with medium intensity in the infrared spectrum corresponds to the band 1005 cm^{-1} observed also with medium intensity in the Raman spectrum and is assigned to ring breathing mode corresponding to 992 $cm^{-1}(a_{1g})$ vibration of benzene.

The four C-H in-plane bending modes are assigned to the infrared bands at 1273, 1172, 1146 and 1067 cm^{-1}. Similarly peaks at 944, 915, 817 and 791 cm^{-1} are assigned to C-H out-of-plane bending modes. These assignments are in good agreement with the assignments given for *m*-difluorobenzene (Green *et al* 1963) and *m*-dichlorobenzene (Scherer and Evans 1963).

The frequencies 1530 and 1357 cm^{-1} observed with very strong intensities in the infrared spectrum of *m*-dinitrobenzene are assigned to asymmetric and symmetric N = O stretching modes respectively. The frequencies 1347 and 837 cm^{-1} are assigned to C-N stretching and NO_2 in-plane bending modes respectively.

p-Dinitrobenzene

The symmetry of this molecule is $D_{2h}(V_h)$. The *z*-axis passes through the NO_2 groups and the *x*-axis is perpendicular to the plane of the molecule. The 30 normal vibrations belong to the following symmetry species :

$$6a_g+1b_{1g}+3b_{2g}+5b_{3g}+2a_u+5b_{1u}+5b_{2u}+3b_{3u}$$

Vibrations belonging to the first four species are Raman active and those belonging to the last three species are infrared active. The a_u vibrations are inactive in both the spectra.

The four C-H stretching frequencies are all expected to lie just over 3000 cm^{-1} but a precise assignment is difficult, since they tend to mask each other and to interact with summation levels of the C = C stretching mode (Lebas and Josien 1956). The strongest Raman line is likely to be due to the a_{1g} frequency and the strongest infrared band to the b_{2u} frequency, since in a crude approximation the b_{2u} bands should be three times as strong as the b_{1u}, because the C-H bonds make an angle of only 30° with the y-axis but 60° with the z-axis. The frequency 3109 is assigned to b_{2u} C-H stretching mode.

The e_{2g} (1585 cm^{-1}) vibration of benzene splits up into a_{1g} and b_{3g} components when the symmetry is reduced from D_{6h} to D_{2h}. The frequency 1585 cm^{-1} is assigned to a_{1g} or b_{3g} component of 1585 cm^{-1} (e_{2g}) C = C vibration of benzene. Similarly the e_{1u} (1485 cm^{-1}) vibration of benzene splits up into b_{1u} and b_{2u} components, when the symmetry is reduced from D_{6h} to D_{2h}. As mentioned above that the b_{2u} component is stronger than the b_{1u} component, the frequencies 1478 and 1382 cm^{-1} are assigned to the b_{1u} and b_{2u} component of e_{1u} (1485 cm^{-1}) C = C vibration of benzene. The benzene vibration 1310 cm^{-1} (b_{2u}) goes to b_{1u} when the symmetry is reduced from D_{6h} to D_{2h}. The frequency 1282 cm^{-1} observed in the Raman spectrum of this compound is assigned to ring breathing mode. These assignments are in good agreement with the assignments given by Stojiljkovic and Whiffen (1958) in the case of p-dihalogenobenzenes.

The three C-H in-plane bending frequencies are characterised by 1358, 1161 and 1104 cm^{-1} vibrations of p-dinitrobenzene. Out of these the frequency 1358 cm^{-1} is assigned to b_{3g} species and the frequencies 1161 and 1104 cm^{-1} to b_{1u} and b_{2u} species respectively.

Similarly the four C-H out-of-plane bending vibrations are not observed in this case. Only three frequencies 906, 800 and 710 cm^{-1} are observed and are assigned to this mode

The frequencies 1552 and 1343 cm^{-1} are assigned to asymmetric and symmetric N = O stretching modes. The frequency 1319 cm^{-1} is assigned to b_{2u} C-N stretching mode and the frequencies 873 and 839 cm^{-1} observed with strong intensities in the infrared spectrum are assigned to NO_2 in-plane bending modes. These assignments are in agreement with the assignments given by Green *et al* (1961) and Stephenson *et al* (1961).

A number of combinations and overtones of the above mentioned vibrational frequencies have also been observed and these are included in their respective Tables.

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